

COMPUTATIONAL CHEMISTRY TOOLKIT FOR ENERGETIC MATERIALS DESIGN

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ABSTRACT

A computational chemistry toolkit is presented, demonstrating the ability to predict properties related to performance or hazard of these materials. The purpose of this toolkit is to allow the design and assessment of advanced energetic materials before investing in synthesis. Newly developed methods are presented to treat emerging exotic high-nitrogen systems considered as candidates for insensitive and environmentally-friendly advanced energetic materials.

1. INTRODUCTION

New computer tools and software developments have made possible “Materials By Design” programs, in which new materials can be computationally constructed and assessed before actual production. National and international investigators from almost every university, institution, research center, and within industry are aggressively engaged in efforts to develop multiscale modeling and simulation methodologies to model and analyze complex phenomena across multiple time and length scales. It is now possible to predict structure/property relationships for both simple and complex materials, as well as predict the dynamic behavior of materials at all relevant length scales, including the more challenging and least empirical atomistic level. However, only in recent years have fundamental theoretical chemistry modeling and simulation tools for energetic materials (EM) research dramatically evolved. These efforts are expected to impact the DOD’s ability to model, analyze, and understand a vast array of energetic materials and complex formulations, leading to a Materials By Design capability in this area.

It is not sufficient, however, simply to collect computational models that predict various properties and processes of interest in a notional material. Rather, a protocol and framework for integration and validation of emerging methods and models for energetic materials design is required. We have designed such a framework within a Computational Chemistry Toolkit for energetic materials design. It is hoped that this toolkit will evolve into a collection of well-integrated multiscale modeling methodologies capable of coupling behaviors from the atomic scale through to the full-scale system. At this time, the majority of our efforts have been devoted to

atomic-level modeling, which will be the focus of this paper.

Significant advances have been made in the development of computational atomistic methods to predict properties related to performance, sensitivity, and environmental impact of a new material. Special attention has been given to the prediction of two properties that are used to provide an initial assessment of the potential performance of a material in a gun or warhead: the heat of formation and the density of the material. Performance metrics (impetus or detonation velocities and pressures) are dependent on the energy content of the charge, reflected by the heat of formation of the energetic material, and the density, which is an indicator of how much material can be packed into the charge. Therefore, a high-density material with a high heat of formation would appear to be a desirable candidate. We have tested and assessed a variety of computational chemistry methods to accurately predict such performance properties for conventional CHNO explosives (Rice, Pai, and Hare, 1999; Byrd and Rice, 2006; Rice and Hare, 2002; Rice and Sorescu, 2004). Unfortunately, until recently there has been no similar collection of computational methods available to predict *a priori* these properties for high nitrogen compounds or for ionic crystals (either high-nitrogen or CHNO salts). Previous tools that have been developed for CHNO containing energetics are completely unsuited for ionic materials, and cannot be assumed to be transferable to high-nitrogen neutrals. Therefore, in such cases, new predictive methods are required. By expanding on earlier methodologies (Baboul et al., 1999), as well as testing alternative methods that are applicable to ionic materials (Jenkins et al., 2002), we are now able to predict the heats of formation and densities of both neutral and ionic high nitrogen materials.

Other aspects of materials that are receiving increased attention are the negative effects of munitions on the environment and the cost associated with both test facility clean-up and disposal of synthesis waste. These have recently been introduced into the factors that are considered before investing in synthesis and testing. Accordingly, we are expanding our program to develop models to address the environmental hazards of energetic materials. Through the use of quantitative structure property/activity relationships (QSPR / QSAR), we have begun investigating possible indicators of mammalian and aquatic toxicity.

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This paper will describe our past and current efforts to further predictive capabilities of energetic materials. This paper will outline the procedures we have investigated in order to predict the heats of formation and densities of both neutral and ionic high nitrogen materials. We will also provide a discussion on limitations on current theoretical tools and subsequent needs and intentions for advancing our models.

2. RESULTS AND DISCUSSION

2.1. Prediction of Crystal Density

Several approaches have been used to predict crystal densities without *a priori* knowledge of the system. The first, and most sophisticated, is that of *ab initio* crystal prediction, in which the crystal microstructure is determined using information about a single, isolated molecule (and requires a description of interatomic interactions). This method and a general CHNO interaction potential were assessed as viable tools for crystalline microstructure (and density) predictions of explosives by Rice and Sorescu (Rice and Sorescu, 2004) through application to a large number (174) of CHNO crystals with energetic functionalities. Eight-five percent of the predictions produced crystallographic parameters and molecular configurations which matched those of the experimental counterpart and were, on average, higher than experiment by less than 3%. The overall good performance of the model demonstrates it is reasonable to use in crystal predictions of similar CHNO systems where the crystallographic symmetry is not known *a priori*. Unfortunately, the method and model have exhibited limitations when applied to emerging novel energetic materials.

Using experimental information generated by T. Klapötke (U. Munich), we established that the aforementioned procedure was unsuitable for prediction of high-nitrogen neutral and ionic crystals. The main limitation of the method and model for treatment of high-nitrogen neutrals was in the force-field. The model used in the earlier study was parameterized to a nitramine crystal, and shown to be transferable to other CHNO systems. Its application to high-nitrogen systems provided disappointing predictions of density. The method as currently formulated accepts only single molecules as the initial packing moiety around which candidate crystal are constructed. Since ionic systems are inherently multi-molecular moieties, this method cannot be currently applied to ionics.

In light of these complications, we explored a new procedure to predict crystal densities using quantum mechanical predictions of the volume of either isolated

molecules or ions. In this procedure the “molecular volume” (or “formula unit volume”, for ionic systems) is used to calculate the crystal density. The molecular volume is that contained within specified isosurfaces of the electron density of the molecule, which can be readily calculated using quantum mechanics. To assess this method for neutrals, we have predicted crystal densities for 181 CHNO species for which experimental crystallographic information exists. Predicted molecular volumes have average and root mean square (rms) deviation from experiment -0.9 and 3.7%, respectively. We note that this method of crystal density prediction produced statistical agreement with experiment as good as those generated in the study of 174 CHNO systems using *ab initio* crystal prediction, at a substantially reduced computational cost (Rice and Sorescu, 2004). We then calculated molecular volumes for eight high-nitrogen neutrals; predicted densities have a 2.7% rms deviation from experiment.

We next used the procedure to predict crystal densities of ionic crystals. As it is not possible to use gas phase quantum mechanical predictions of isolated ionic partners to determine their most probable relative arrangement in the crystal, (and thus, the volume of the pair) the volume of the formula unit M_pX_q (where M denotes the cation and X denotes the anion) is defined as:

$$\text{Volume} = pV_+ + qV_- \quad (1)$$

Our assessment of this method was attempted for 34 high-nitrogen ionic salts provided by Klapötke (U Munich); a comparison of the predicted and experimental molecular volumes are given in Fig. 1. Predicted crystal densities using this method had a 4.2% rms deviation from experiment.

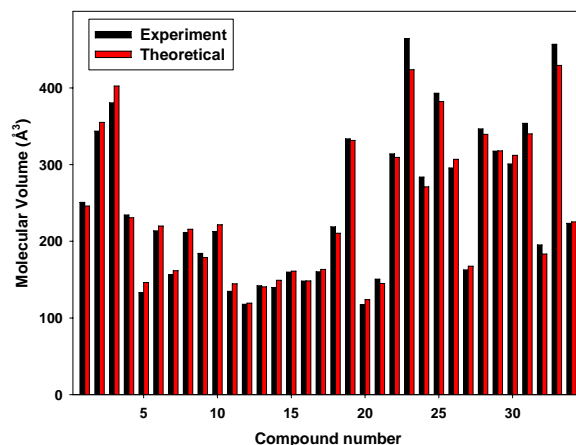


Figure 1. Experimental and theoretical molecular volumes for 34 high nitrogen salts.

2.2. Prediction of Heats of Formation

Most energetic materials exist in the solid phase, and their heats of formation in this phase are a property that cannot be directly calculated using quantum mechanical theory. However condensed phase heats of formation can be obtained if cohesive energies can be determined and combined with quantum mechanical predictions of gas phase heats of formation. For neutral molecules, the cohesive energy of a solid is roughly that of the heat of sublimation; for ionic crystals, the cohesive energy is the lattice energy.

Using a procedure developed by Politzer (Poltzer, 1994), we have parameterized equations that are used to predict the heats of sublimation and vaporization using QM information for an isolated molecule of a neutral crystal (Rice, Pai, and Hare, 1999; Byrd and Rice, 2006). We combined this information with predicted gas-phase heats of formation of a series of CHNO systems using atom equivalents (Rice, Pai, and Hare, 1999). While this work demonstrated the utility of the method, the error associated with the solid phase heats of formation compelled us to improve its accuracy. In a subsequent study, we expanded our calculations to use a larger basis set and group equivalents (Byrd and Rice, 2006). The resulting rms and maximum deviation of predicted solid heats of formation were reduced by approximately 40%.

It could not be assumed that these computational tools, parameterized using experimental information for CHNO systems, would be transferable to high-nitrogen systems. In fact, application of the tools to a newly-synthesized high-nitrogen compound (1-Methyl-5-(methylnitramino)-1*H*-tetrazole) (Karaghiosoff et al., 2006) predicted a solid phase heat of formation of 70.1 kcal/mol, far larger than the measured value (2.8 kcal/mol). Since this was the first application of our tool to a high-nitrogen compound, we did not have reason to have confidence in the computational tool for use in predicting solid phase heats of formation for high nitrogen neutrals. Therefore, we were forced to try to identify and remedy the most probably source of error to allow application to high-nitrogen systems.

Values for heats of sublimation of the CHNO crystals we surveyed typically range between 10-30 kcal/mol, with very few systems falling outside this range. Additionally, we know that the heat of sublimation must always be positive. Conversely, experimental gas phase heats of formation for the CHNO systems we have surveyed fall within a much larger range (from -70 to +100 kcal/mol) (Byrd and Rice, 2006). In considering the disagreement of our tool with the measured results for 1-Methyl-5-(methylnitramino)-1*H*-tetrazole, we concluded that the major source of any discrepancy in our calculations and the measured value would be in the value of the gas phase heat of formation. Thus, we focused on exploring whether the error in the calculation of the solid

phase heat of formation might be due to improper prediction of the gas phase heats of formation. Therefore, we pursued other quantum-mechanically based methods for predictions of this thermodynamic value. In all calculations reported hereafter, the heats of sublimation were calculated using the aforementioned method (Byrd and Rice, 2006).

The alternative methods we are using for predicting gas phase heats of formation are variants of the popular G3 methods specifically the G3(MP2) (Curtiss et al., 1999) and G3(B3LYP) (Baboul et al., 1999) approaches. The G3(MP2), G3(B3LYP) and previously-discussed atom/group equivalent methods were used to calculate the gas phase heats of formation of a set of neutral high nitrogen crystals and added to the predicted heats of sublimation. The results are compared with experiment in Figure 2. For all compounds, the theoretical methods are in reasonable agreement with each other; additionally, all calculated values are in agreement with experiment except for Compound 2 (1-Methyl-5-(methylnitramino)-1*H*-tetrazole) (Karaghiosoff et al., 2006). This suggests that either re-measurement of the heat of formation of Compound 2 should be performed or that there is something within this system that is not captured by the quantum mechanical calculations. We emphasize that the two quantum mechanical approaches (atom/group equivalents versus G3 methods) are sufficiently dissimilar that it is extremely unlikely that the error is within the predicted gas phase heat of formation. There is a possibility, of course, that the heat of sublimation is poorly predicted for this system. That would not, however, explain the large discrepancy between the theoretical values and the measured result for Compound 2.

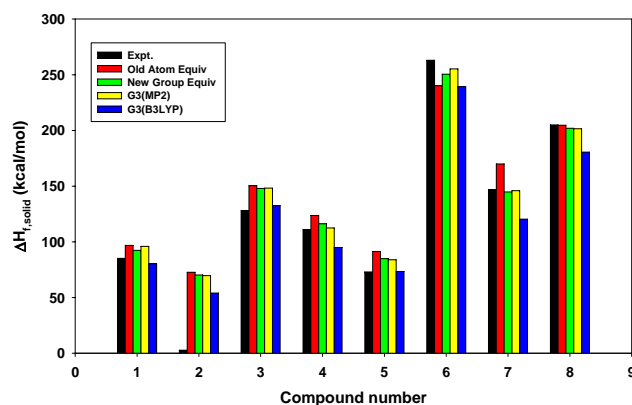
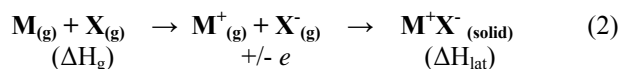


Figure 2. Solid phase heats of formation for high-nitrogen crystals. Experimental values are taken from Karaghiosoff et al., 2006 and Huynh et al., 2005. “Old Atom Equiv” denotes calculations using the atom equivalent method described in Rice et al., 1999. “New Group Equiv” denotes calculations using the group equivalent method described in Byrd and Rice, 2006.

The calculation of heats of formation for ionic solids is substantially different than that discussed previously for neutral crystals. The heat of formation of ionic compounds is determined using Born-Haber Cycles in which a series of reactions involving the ionic components are employed to produce the overall final result. The user is free to choose any series of reactions in the Born-Haber Cycle that will lead to the formation of the ionic crystal; we have chosen the following:



This cycle consists of three steps in which formation energies for each of the components can be calculated. The first step (Step 1) requires the evaluation of the gas phase heats of formation of the neutral form of the charged components. The formation energies for the ionic components are then determined by evaluating the electron affinity or ionization energies and adding these to the heats of formation of the neutral moieties (Step 2). The third step of the cycle requires the evaluation of the lattice enthalpy (Step 3). The main drawback to this approach is the requirement that the neutral form of the charged species must be a minimum on the potential energy surface (PES). If it is not, then our Born-Haber Cycle would require inclusion of reactions leading to the neutral moieties in Step 1.

Unfortunately, there are limited (if any) experimental data that can be used to assess the quality of the calculations associated with each step in the aforementioned cycle. We are limited to comparing the overall final result with the experimental value of the heat of formation of the ionic crystal. This makes establishing the sources of errors in this cycle complicated.

For Step 1, a G3-type approach as described above was used to predict the gas phase Heat of Formation for the ionic species. Step 2, the evaluation of the Ionization Energy/Electron Affinity, was performed by calculating the energy difference between the neutral form of the ionic component and that of the ionized versions. In both cases, it is imperative that the geometries are optimized, since in many cases, the molecular structures for the neutral forms of the ions are substantially different than the ionic forms. In evaluating 20 cations and 6 anions used in high-nitrogen ionic crystals provided by Klapötke (U Munich) we found that half of the compounds had structural relaxation energies on the order of 50 kcal/mol.

The final step in the evaluation of the Born-Haber cycle is the determination of the lattice enthalpy, a measure of the energy required to dissociate the ionic crystal into its gaseous ions. The magnitude of this energy is quite large compared to the weaker intermolecular cohesive energies associated with organic

molecular crystals (which are due mainly to van der Waals interactions), since it is a result of numerous long-range electrostatic interactions of ionic partners within the crystal. This value can be directly calculated by simply adding up all interatomic interactions within the crystal lattice if the microstructure of the ionic crystal and a reasonable description of the interatomic interactions are known. Unfortunately, these two requirements are not always available; further, it is preferable to have a methodology for predicting this value that does not rely on experimental data. Toward this end, Jenkins *et al.* (Jenkins *et al.*, 1999; Jenkins *et al.*, 2002) developed an equation that correlates the inverse cube root of the molecular volume of the formula unit of an ionic crystal M_pX_q with its lattice potential energy $U_{\text{pot}}(\text{M}_p\text{X}_q)$. Jenkins *et al.* parameterized the functional form for U_{pot} using lattice potential energies from a previous work of Jenkins (Jenkins, 1998). These data consist of values derived from thermochemical cycles using experimental information and those from full scale calculations of the lattice potential energy of a crystal and the information used in the parametrization was limited to salts containing alkali metal and alkaline earth cations (Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba). Several possible sources of errors exist for this approach in its application to the high-nitrogen compounds we are evaluating, including the variable reliability of fitting data (lattice energies) and assumption of the ionic volumes used in the parameterization. In the Jenkins approach, the cations are very small, single spherical elements, whereas many of the cations in the high-nitrogen salts are very large.

Because there is no way in which the Jenkins *et al.* approach can be assessed directly, we can only compare the summed energies of the Born-Haber cycle with the few experimental data we have:

Table 1. Experimental versus Theoretical for Solid Phase Heats of Formation.

Species	$\Delta H_{\text{fMX(s)}} \text{ (kcal/mol)}$		
	Experiment ^a	Theoretical ^a	This Work
1-5-Diamino-4-methyl-tetrazolium nitrate	8.4	41.7	47.5
1-5-Diamino-4-methyl-tetrazolium azide	138.1	161.6	165.4
1-5-Diamino-4-methyl-tetrazolium dinitramide	45.3	92.1	94.9

^a Experimental and theoretical column values from Gálvez-Ruiz *et al.*, 2005.

Note that the theoretical result generated by Gálvez-Ruiz *et al.* (Gálvez-Ruiz *et al.*, 2005) invoked a Born-Haber cycle using reactions along with proton affinities, whereas we utilize the procedure outlined above. Additionally, the Gálvez-Ruiz *et al.* calculations used the G2 method (Curtiss *et al.*, 1991), which has different empirical corrections and approaches than the G3 methods we used. Note that the two theoretical approaches, which would have distinctly different sources of error, are very close in value for the three compounds. They both, however, overshoot the experimental values by 30-40 kcal/mol. Since the common element between the two theoretical methods is the Jenkins method for predicting lattice energies, we suspect the source of error, if any, is in this step.

2.3. Prediction of Aquatic Toxicity

There exists no single test which constitutes a standard indicator of aquatic toxicity, and previous theoretical and experimental studies on energetic materials have been performed on a variety of species. However, the Environmental Protection Agency (EPA) has greatly facilitated the analysis of aquatic toxicity by developing the Fathead Minnow Acute Toxicity Database (EPAFHM). This freely available online database encompasses homogeneous-assay Fathead Minnow (*Pimphales promelas*) LC50 toxicity data collected for over 600 industrial organic chemicals, and is an invaluable resource for the QSAR (quantitative structure activity relationship) practitioner (Russom, 2003). We use selected data from the EPAFHM in conjunction with the commercial QSAR package CODESSA 2.7.2 (CODESSA, 2005) to develop a 5-parameter predictive equation for Fathead Minnow LC50 toxicity.

To develop this expression, 87 compounds were chosen from the EPAFHM according to a few key selection criteria. No compounds containing halogens were selected on the basis that halogen-containing systems present a different mode of action for toxicity and are outside the realm of interest for these systems. Compounds containing nitro groups in as many different topologies as possible were chosen to capture as much as possible the effect of nitro group placement. Finally, emphasis was given to compounds containing nitrogen in many different chemical environments. The CODESSA package was used to perform a best multilinear regression analysis on hundreds of descriptors (parameters) to determine the best expression to predict Fathead Minnow LC50. Calculated values from the resulting expression versus experimental Fathead Minnow LC50 values for this 87 compound training set are shown in Fig. 3. Results are highly satisfactory, where the resulting square of the regression correlation coefficient R^2 is 0.8407 (indicating a high degree of correlation between predicted and experimental values) and the root mean squared error

(RMSE) is 0.3901, an acceptable margin of error for these purposes. The parameters used in this correlation include the octanol-water partition coefficient (the sole experimentally derived parameter in the expression, and a common component of biological correlation expressions) and several quantum-chemically derived parameters relating to reactivity of chemical moieties within the molecule.

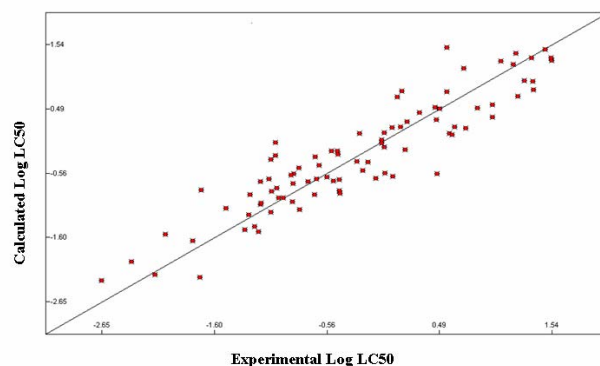


Figure 3. Calculated vs experimental fathead minnow LC50 toxicities for the 87-compound training set.

It has been assumed for the purposes of this project that a sufficient level of accuracy is to be able to predict the LC50 value to within a factor of three (or equivalently, a LogLC50 value to within 0.5 log units). The results shown demonstrate that toxicities for the vast majority of the chosen compounds are predicted with this level of accuracy. Assessment of the largest outliers (compounds whose predicted values are outside of this range of accuracy) show no trends in chemical group or mode of toxicity. This QSAR is currently being tested on known and notional energetic materials to validate its inclusion as part of the computational chemistry toolkit.

CONCLUSIONS

We have described a newly-developed computational toolkit composed of models for the prediction of properties of energetic materials related to performance and environmental hazard. These tools can be used in the design, characterization and assessment of a material without the need for synthesis and measurement. Our intention is to augment the toolkit with a variety of critical models in order to simulate and analyze complex phenomena across multiple time and length scales.

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